

## Lecture 23

# OXIDATION AND PHOTOLYSIS (1)

Course: Water Reuse  
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## Chemical oxidation

- Processes in which oxidizing chemicals are added to water that directly react with the constituents in water are known as conventional oxidation processes.
- Processes in which oxidizing chemicals are added to water to cause the formation of hydroxyl radicals (OH·), which then react with the constituents in water, are known as advanced oxidation processes (AOPs).
- A dot is added after the radical species to show that there is an unpaired electron in the outer orbital. The key difference is the power of the oxidizing agent, known as the oxidation potential.

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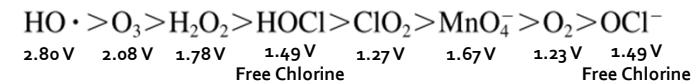
## Applications

- Chemical oxidation can have various goals, including:
  - (1) odor control
  - (2) hydrogen sulfide control
  - (3) color removal
  - (4) iron and manganese removal
  - (5) disinfection
  - (6) control of biofilm growth and biofouling in treatment processes and distribution system components
  - (7) oxidation of selected trace organic constituents

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## Oxidation rate and potential

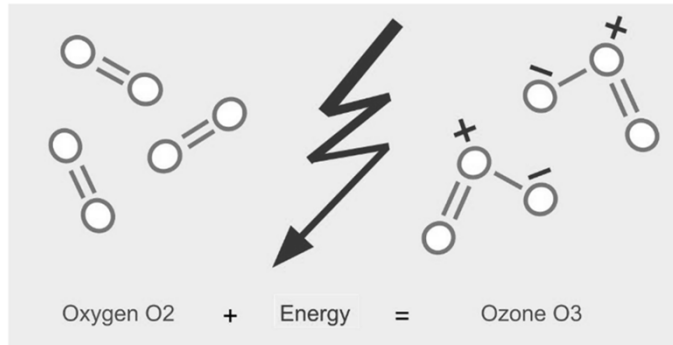
- The rate of oxidation (how fast the oxidant is used up) typically follows the trend given below; however, there will be exceptions depending on the characteristics of the solution (e.g., pH) and type of target compound:



- The driving force for the exchange of electrons between an oxidant and a reductant is the difference in their electrical potentials (oxidants have highly positive potentials = they want to receive electrons)

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## Ozone generation

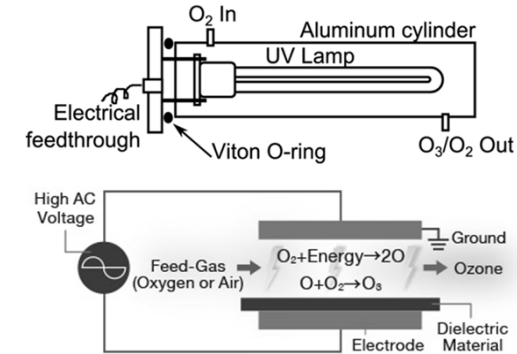


In nature ozone is created during thunderstorms when lightning strikes. UV light from the sun is also able to provide energy to create ozone from oxygen

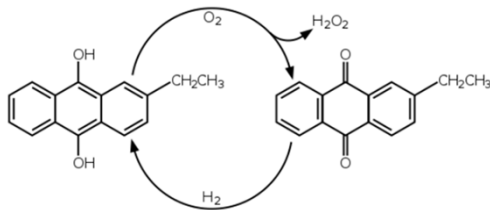
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## Ozone generation

O<sub>3</sub> can form by corona discharge or UV bombardment

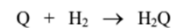


## Hydro



### Step 1 - Hydrogenation

Palladium catalyses the reaction between H<sub>2</sub> and anthraquinone to create anthrahydroquinone (H<sub>2</sub>Q):

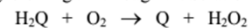


### Step 2 - Filtration

The palladium catalyst is filtered out of the solution.

### Step 3 - Oxidation

The solution is oxidised by blowing air through the solution, forming the H<sub>2</sub>O<sub>2</sub>:



### Step 4 - H<sub>2</sub>O<sub>2</sub> Extraction

The hydrogen peroxide is removed in a liquid-liquid extraction column and concentrated by vacuum distillation.

## Oxidation byproducts

- Aside from the expense of chemical oxidation, the primary concern with any chemical process is the potential for the formation of toxic byproducts
- This can happen due to incomplete oxidation. While the AOPs (hydroxyl radical oxidation processes) are able to achieve complete oxidation under optimal conditions, conventional chemical oxidation is typically not powerful enough to reach this endpoint.
- Therefore, subsequent treatment processes may be needed to remove the oxidation byproducts, such as adsorption.

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## Oxidation byproducts

- Chemical oxidation increases the biodegradability of some constituents, meaning that some organics which were not available as food to microorganisms, now become available.
- This potentially requires the use of a biological process to remove residual biodegradable organic material.
- Byproduct formation may be controlled by removal of the byproduct precursors before application of the oxidant and careful control of the oxidant dose.

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## AOP

- Advanced oxidation processes can generate elevated concentrations of hydroxyl radical (HO•) and can be used to destroy trace constituents that cannot be oxidized completely by conventional oxidants.
- The hydroxyl radical is a strong oxidant capable of the complete oxidation of most organic compounds into carbon dioxide, water, and mineral acids (e.g., HCl).
- Because of the unpaired electron, hydroxyl radicals are reactive electrophiles (electron-loving) that react rapidly with nearly all electron-rich organic compounds thereby breaking bonds

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## AOP

- Advanced oxidation processes differ from the other treatment processes discussed (such as adsorption, ion exchange, or stripping) because organic compounds in water are degraded rather than concentrated or transferred into a different phase.
- Because a secondary waste stream is not generated, there is no additional cost to dispose of or regenerate materials. Hydroxyl radicals are NON SELECTIVE, i.e. capable of oxidizing almost all reduced materials present without restriction to specific classes or groups of compounds, as compared to other oxidants.

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## Mechanisms of hydroxyl radical attack

### 1. By radical addition

The addition of the hydroxyl radical to an unsaturated aliphatic or aromatic organic compound (e.g., C<sub>6</sub>H<sub>6</sub>) results in the production of a radical organic compound that can be oxidized further by compounds such as oxygen or ferrous iron to produce stable oxidized end products. Radical addition is much more rapid than hydrogen abstraction. In the following reactions the abbreviation R is used to denote the reacting organic compound.



### 2. By hydrogen abstraction

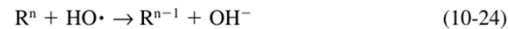
The hydroxyl radical can be used to remove a hydrogen atom from organic compounds. The removal of a hydrogen atom results in the formation of a radical organic compound, initiating a chain reaction where the radical organic compound reacts with oxygen, producing a peroxy radical, which can react with another organic compound.



## Mechanisms of hydroxyl radical attack

### 3. By electron transfer

Electron transfer results in the formation of ions of a higher valence. Oxidation of a monovalent negative ion will result in the formation of an atom or a free radical. In the following reaction, n is used to denote the charge on the reacting organic compound R.



### 4. By radical combination

Two radicals can combine to form a stable product.



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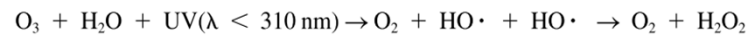
## Notes

- Unfortunately, because the half-life of the hydroxyl free radicals is short, on the order of microseconds, it is not possible to develop high concentrations.
- With extremely low concentrations, the required detention times for microorganism disinfection, based on the  $C_R t$  concept, are prohibitive.
- AOPs are usually applied to low COD reclaimed waters (following other treatment) because of the costs of generating the hydroxyl radicals.
- Most common technologies: ozone/UV, ozone/ $H_2O_2$ ,  $H_2O_2$ /UV.

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## AOP: Ozone/UV

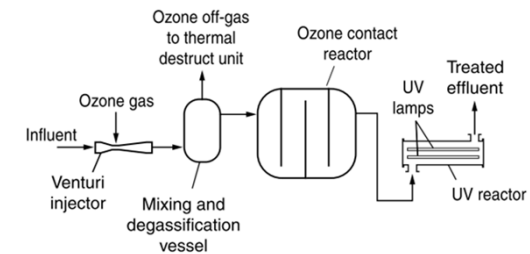
- The photolysis of ozone in wet air results in the formation of hydroxyl radicals. In water, the photolysis of ozone leads to the formation of hydrogen peroxide, which is subsequently photolyzed or reacted with  $O_3$  to form hydroxyl radicals. The ozone/UV process can degrade compounds through direct ozonation, photolysis, or reaction with the hydroxyl radical



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## AOP: Ozone/UV

- Ozone and UV dosages in the range of 16-24 mg/L and 810-1610 mJ/cm<sup>2</sup>, respectively, are much stronger the use of either UV or  $O_3$  alone. As with all UV processes, fouling of the UV lamp sleeve, lamp replacement costs, and energy consumption are important considerations.



## AOP: Ozone/H<sub>2</sub>O<sub>2</sub>

- For compounds that do not adsorb UV or where the transmittance of the water to be treated inhibits photolysis, AOPs involving ozone/H<sub>2</sub>O<sub>2</sub> may be more effective than ozone/UV.



- According to the equation, 0.5 mols of H<sub>2</sub>O<sub>2</sub> are needed for every mol of O<sub>3</sub> or a mass ratio of 0.354 kg of H<sub>2</sub>O<sub>2</sub> is needed for every kg of O<sub>3</sub>. However, there are several issues that impact the proper dosages of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>

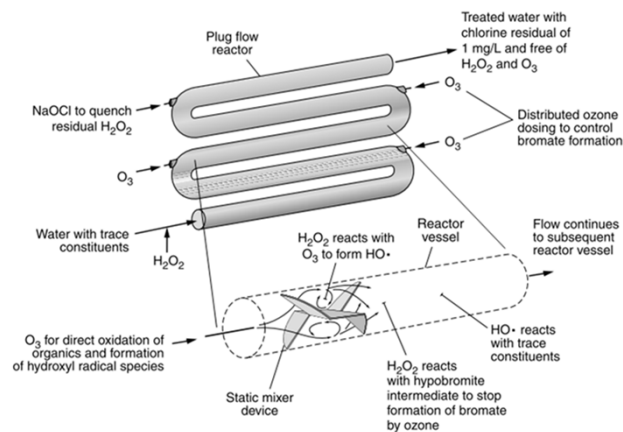
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## AOP: Ozone/H<sub>2</sub>O<sub>2</sub>

- O<sub>3</sub> tends to be more reactive with background organic matter and inorganic species than H<sub>2</sub>O<sub>2</sub>. As a result, the required O<sub>3</sub> dosage will be higher than estimated from stoichiometry. Pilot studies are usually conducted to determine the chemical dosage required
- Typical ozone and hydrogen peroxide concentrations range from 5-30 mg/L and 5-15 mg/L, respectively. Having excess O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> can cause problems of byproduct formation, quenching HO· radicals, etc.

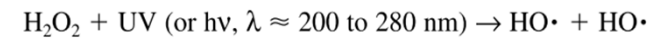
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## AOP: Ozone/H<sub>2</sub>O<sub>2</sub>



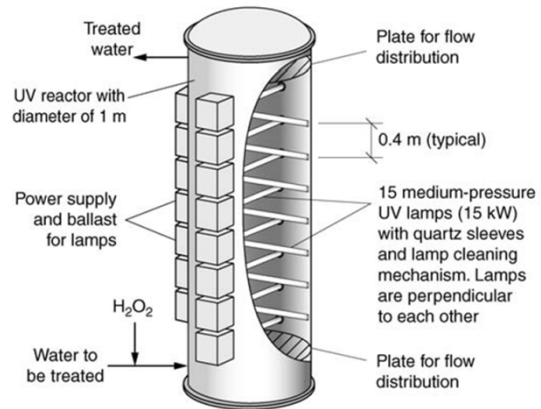
## AOP: H<sub>2</sub>O<sub>2</sub>/UV

- HO· is also formed when water containing H<sub>2</sub>O<sub>2</sub> is exposed to UV light. The following reaction can be used to describe the photolysis of H<sub>2</sub>O<sub>2</sub>:



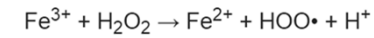
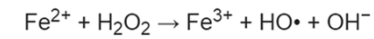
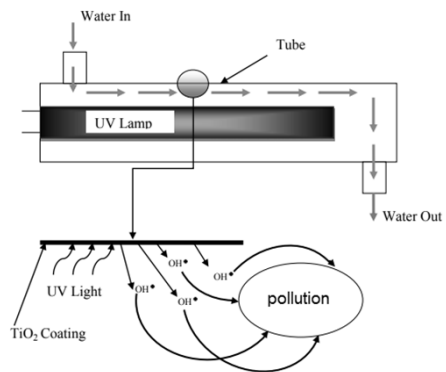
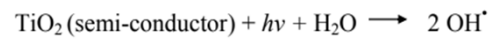
- This process is not common for potable water because it normally results in high effluent H<sub>2</sub>O<sub>2</sub> concentrations (due to high dosage required at inlet). The residual H<sub>2</sub>O<sub>2</sub> consumes chlorine and interfere with disinfection. However, the residual hydrogen peroxide is not a concern in water reclamation.

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AOP: H<sub>2</sub>O<sub>2</sub>/UVDr. Alireza Bazargan [info@environ.ir](mailto:info@environ.ir)

## AOP: Fenton's reagent

- Iron(II) is oxidized by hydrogen peroxide to iron(III), forming a hydroxyl radical and a hydroxide ion in the process. Iron(III) is then reduced back to iron(II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical and a proton. The net effect is a disproportionation of hydrogen peroxide to create two different oxygen-radical species, with water (H<sup>+</sup> + OH<sup>-</sup>) as a byproduct:

Dr. Alireza Bazargan [info@environ.ir](mailto:info@environ.ir)AOP: TiO<sub>2</sub>/UV

## Comparison

5 = very good, 1 = very bad

Parameters	AOPs					
	O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub>	O <sub>3</sub> /UV	H <sub>2</sub> O <sub>2</sub> /UV	TiO <sub>2</sub>	Fenton
Mechanical Reliability	4	4	3	3	2	2
Process Reliability	4	4	4	4	2	2
Flexibility	4	4	4	4	3	3
Adaptability	3	3	2	2	3	3
Energy Consumption	2	3	2	4	2	5
Average Engineering	3.4	3.6	3	3.4	2.4	3
Climate Change	2	3	2	4	2	5
Eutrophication	5	5	5	5	5	5
Toxicity	2	3	2	3	2	2
Average Environmental	2.25	2.75	2.25	3	2.25	3
Public Acceptance	4	4	4	4	2	2
Ease of Use	4	4	4	4	2	2
Economic Feasibility	5	4	4	3	1	4
Average Economic and Social	4.33	4	4	3.67	1.67	2.67
Comprehensive Average	3.33	3.45	3.08	3.36	2.11	2.89